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Correlation of Microbial Degradation Rates with Chemical Structure

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Correlation of Microbial Degradation Rates with Chemical Structure

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■ Structure–reactivity relationships are established for the microbial degradation of selected organic compounds. Second-order microbial degradation rate constants determined in natural water samples for six compounds correlate with the second-order alkaline hydrolysis rate constants. Also, second-order microbial degradation rate constants for four phthalate esters obtained with organisms from sediment–water samples correlate with the second-order alkaline hydrolysis rate constants. Similar correlations are demonstrated for the rates of oxidation of substituted phenols by mixed microbial cultures isolated from soils and Hammett σ constants.

Correlations between rate constants for specific chemical reactions and values for a selected physical or chemical property of the organic compounds are well established in the chemical literature (*1*). Such correlations can be used to predict rate constants required to assess the behavior of organics in aquatic environments (*2, 3*). Similar correlations of enzyme-catalyzed reactions, although often more complex, have also been demonstrated (*1, 4*). Several studies have addressed the effect of chemical structure on susceptibility to microbial breakdown using bacteria isolated from soils (*5, 6*) and natural waters (*7, 8*), but, unfortunately, the correlations have not been successful. The major difficulty with these studies has been the choice of a measurement of biological reactivity to use in the correlation.

Recent studies of the kinetics of microbial degradation of organics in natural water samples provide a data base of rate constants that can be used to examine the relationship of chemical structure to microbial degradation. In these studies, Paris and co-workers (*9–11*) applied a second-order rate expression to describe the rate of disappearance of certain organics mediated by microorganisms in natural water samples. Linear regression analysis using the second-order rate constants, k_b (L org^{-1} h^{-1}), determined in these investigations and the corresponding second-order alkaline hydrolysis rate constants, k_{OH} (M^{-1} s^{-1}), reported by Wolfe and co-workers (*11–15*) gives the correlation described by the linear equation (*16*):

$$\log k_b = m \log k_{OH} + c \qquad (1)$$

Values of m and c along with standard errors of the estimates and the correlation coefficient, r^2, are given in Figure 1. (The second-order biolysis and hydrolysis rate constants for methyl benzoate and anisate according to Wolfe and Paris (*11*) are 7.0×10^{-13} and 5.4×10^{-13} L org^{-1} h^{-1} and 5.0×10^{-3} and 1.1×10^{-2} M^{-1} s^{-1}, respectively.) For this group of compounds, 97% of the variance in the data is accounted for by alkaline hydrolysis. In addition, the F value is 141, which is significant at the greater than 99% confidence level (CL). The correlation (R^2) is improved by inclusion of a second parameter, the octanol–water partition coefficient (K_{ow}) (*17*), which has been postulated to be proportional to the binding strength of a compound at the reaction site (*4*) or proportional to biosorption by organisms (*18*). (Octanol–water partition coefficients were calculated using the transposed linear equation, $\log K_{ow} = -0.653 \log s + 0.880$, obtained by linear regression analysis of the data in ref *17*.) The resulting equation is:

$$\log k_b = m \log k_{OH} + n \log K_{ow} + c \qquad (2)$$

With the inclusion of K_{ow} as a dependent variable, the multiple linear regression coefficient, R^2, is 0.988, which accounts for an additional 2% of the variance of the data. The values of m, n, and c are 0.53 ± 0.03, 0.13 ± 0.06, and -11.8 ± 0.2, respectively. However, the F test shows that inclusion of K_{ow} as a dependent variable after K_{OH} is not significant.

A similar correlation is also shown for phthalate esters. The second-order disappearance rate constants reported by Steen et al. (*19*), for the microbial degradation of four phthalate esters by organisms from sediment samples, and the second-order alkaline hydrolysis rate constant for the corresponding esters reported by Wolfe et al. (*20*) were correlated by use of Equation 1. (Reference *19* contains the biolysis rate constant for di-*n*-butyl phthalate and a description of the experimental methodology and calculations. Second-order biolysis rate constants for the dimethyl, di-*n*-octyl, and bis(2-ethylhexyl) phthalates are 5.2×10^{-9}, 3.1×10^{-13}, and 4.2×10^{-15} L org^{-1} h^{-1}, respectively.) Linear regression analysis of the data gives the values shown in Figure 2 ($r^2 = 0.933$). In addition, the F value is 27.7, which shows that the correlation is significant at the 95% CL. Although 93% of the variance is accounted for by alkaline hydrolysis, the correlation is improved by using Equation 2 ($R^2 = 0.994$). Thus, the octanol–water partition coefficient as an independent variable accounts for an addi-

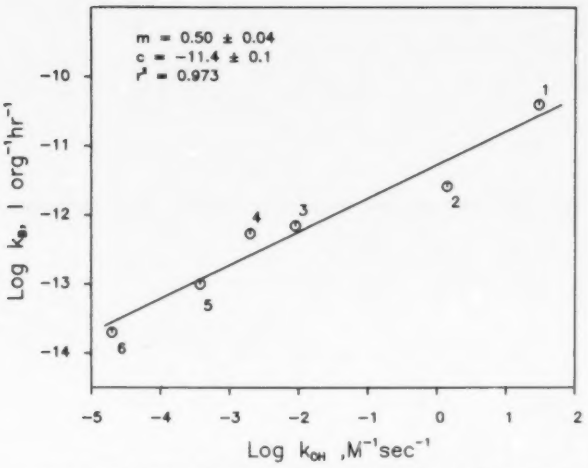

Figure 1. Correlation of second-order alkaline hydrolysis rate constants determined in distilled water at 27 °C with second-order biolysis rate constants determined in natural water samples at 25 °C. The compounds are: (1) *n*-butoxyl ethyl ester of 2,4-D; (2) malathion; (3) methyl benzoate; (4) methyl anisate; (5) methoxychlor; (6) chlorpropham

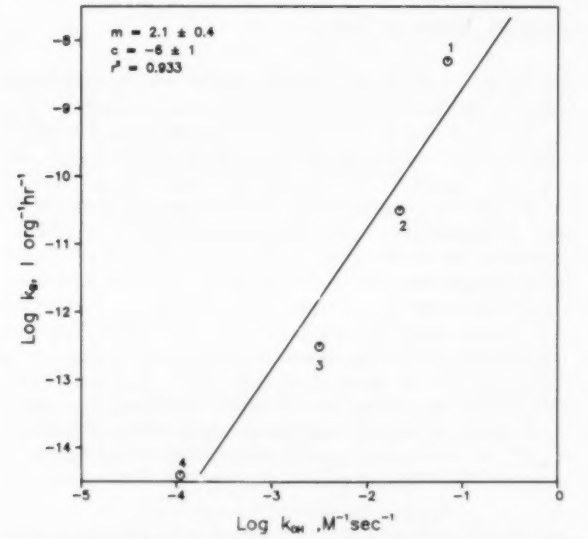

Figure 2. Correlation of second-order alkaline hydrolysis rate constants obtained in distilled water at 30 °C with second-order biolysis rate constants determined at 25 °C: (1) dimethyl phthalate; (2) di-*n*-butyl phthalate; (3) di-*n*-octyl phthalate; (4) bis(2-ethylhexyl) phthalate

tional 7% of the variance. The values of m, n, and c are 1.1 ± 0.3, -0.90 ± 0.3, and -5.1 ± 0.6, respectively. However, the F test shows that inclusion of K_{ow} as a dependent variable in addition to K_{ow} is not significant.

Support for such correlations is obtained from two other studies: the degradation of pesticides in soils and the microbial degradation of phenols in aqueous solution. In the first case, Igarashia et al. (*21*) studied the degradation of five carbamate pesticides in flooded rice soil. Although the study did not differentiate between chemical and biological processes, microbial degradation was postulated, and the authors reported a correlation between the observed first-order disappearance rate constants in the soils and the second-order alkaline hydrolysis rate constants.

Further evidence to support the feasibility of this approach is obtained by analysis of the data reported by Tabak et al. (*22*) on the microbial degradation of substituted phenols. In these studies, the authors presented data on the oxidation of substituted phenols by mixed cultures of bacteria isolated from soils. Unfortunately, kinetic expressions were not developed for the process, but, using their data for initial concentrations of 100 ppm and a 180-min time interval, rates of disappearance can be calculated. The log of these rates (v) for the ortho- and meta-substituted phenols correlated with the Hammett σ constants (Equation 3), where σ is the substituent constant, ρ the slope, and v_0 the rate of the unsubstituted phenol (*7*).

$$\log v = \rho\sigma + \log v_0 \qquad (3)$$

Inspection of a plot of the data and the results from linear regression analysis suggests two separate linear relationships. One is for the methyl- and hydroxy-substituted phenols ($\rho = 0.058 \pm 0.002$, $\log v_0 = 1.99 \pm 0.01$, $r^2 = 0.836$), and the other is for chloro- and nitro-substituted phenols ($\rho = -0.50 \pm 0.05$, $\log v_0 = 1.92 \pm 0.08$, $r^2 = 0.951$).

Even though there are some obvious mechanistic implications concerning the microbial degradation process, it is important that these correlations offer some insight into a method of predicting microbial degradation rate constants in natural waters and maybe even soils. If subsequent studies confirm general applicability of such structure–reactivity relationships and the variance of these biodegradation rate constants from one natural water to another is not too large, as evidenced by recent data of Paris et al. (*11*), then the environmental scientist will have a powerful tool for assessing biotransformation.

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